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Photonic, spectroscopic properties and electronic structure of PTCDI-C8 organic nanostructure

Bayram Gündüz[a], Mustafa Kurban[b,*]

[a] Department of Science Education, Faculty of Education, Muş Alparslan University, 49250 Muş, Turkey
[b] Department of Electronics and Automation, Ahi Evran University, 40100 Kırşehir, Turkey

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ABSTRACT

The changes in the structural, electronic, vibrational and photonic properties of *N*,*N*′-Dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) one-dimensional nanostucture have been investigated using experimental and theoretical techniques. The semi-empirical relations have been proposed for the calculation of the refractive index (n)from its measured and calculated energy gap (E_g) data. FT-IR and FT-Raman spectra characteristics and structural, spectroscopic and electronic properties such as HOMO-LUMO energies, harmonic frequencies, Mullkien atomic charges, dipole moments, radial distribution functions (RDFs) and coordination number of binary interactions were recorded with the aid of density functional theory (DFT) based on optimized structure for gas phase and different solvent environments. Moreover, ultraviolet-visible (UV–vis) spectral analysis and energy gaps has been carried out using experimental techniques and time-dependent (TD) DFT calculations. The results herein obtained reveal that PTCDI-C8 material is suitable for sensitivity applications due to its appropriate optoelectronic paramaters.

1. Introduction

Recently, organic semiconductors have widely used in many electronic, optoelectronic, and photonic applications [1] such as solar cells [2–5] photovoltaics [4,5] light emitting diodes [4,6] sensors [7,8], chemical sensors [9], vapour sensors [10], gas sensors [11,12] and photodetectors [13]. Among organic semiconductors, the perylenediimides (PTCDIs) have attracted great interest in the fabrication of optoelectronic devices such as transistors, light-emitting diodes and photovoltaic cells [14] becuse of their high thermal and photo-stability properties under visible light beam [15–22].

In the literature, a series of available perylene and its derivatives (PTCDI-M, where M = C5, C8, C10, BP2C10, OSC etc.) were studied in various electronic, photovoltaic and optoelectronic devices. Among these derivatives, *N*,*N*′-Dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) is a very important material for organic field effect transistors [23] and solar cells [24,25] as its mobility is higher than that of fullerenes. In this regard, various studies have been conducted on PTCDI-C8 nanostructure. For example, the effect of the thickness on the structural and optical properties of PTCDI-C8 thin films have been investigated using thermal evaporation technique and observed the high degree of molecular packing depending on the optical and structural properties [26]. PTCDI-C8 nanoribbons have been synthesized to investigate nonlinear optical properties for potential applications [27]. The molecular structure of PTCDI-C8 on different substrates has also been reported [28]. In addition, PTCDI-C8 have been performed as an acceptor material for photovoltaic and thin film transistor applications due to its better absorption properties [23,25,29].

The solute-solvent interactions are crucial to understand molecular behaviour because the interactions give rise to the significant changes in the chemical and physical characteristics of the solute from gas phase to solvent phase [30]. In the recent years, thermally evaporated PTCDI-C8 thin films with four different solvents (methanol, acetone, chlorobenzene, chloroform) have been experimentally researched [31]. In the study, the methanol treated vertical nanostructure was found to give the best efficiency on the solar cell performance. Therefore, the contributions from different physical and optoelectronic properties based on different solvent environments have still to be discussed. In this regard, the aim of the present study is to evaluate photonic, spectroscopic properties and electronic structure of PTCDI-C8 nanostucture using experimental technique and density functional theory (DFT)

* Corresponding author.
E-mail addresses: mkurbanphys@gmail.com, mkurban@ahievran.edu.tr (M. Kurban).

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approach. These properties were controlled with different solvents (ethanol, methanol, and chloroform). Firstly, we have analysed the Fourier Transform Infrared (FT-IR) and Fourier Transform Raman (FT-Raman) spectra characteristics, radial distribution functions (RDFs) and probability distributions in terms of coordination number of the binary interactions, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the frontier molecular orbital energy gap (HOMO–LUMO difference in energy gap, E_g), Mullkien atomic charges of the small molecule using DFT calculations. The measured and calculated $E_g$values have been performed for different solvents. Using time-dependent (TD)-DFT method, the theoretically predicted the ultraviolet-visible (UV–vis), HOMO, LUMO and E_g of the nano-structure have been compared with the measured results. Different relations were also performed to calculate the optical refractive index (n) values and compared with measured values for different solvents. Later, the effects of the solvents on the mass extinction coefficient, $(\alpha h\vartheta)^2$curves based on photon energy (E), single oscillator energy (E_0), dispersion energy (E_d), constrat based on E, surface and volume energy loss functions (SELF and VELF) depend on the dielectric constant were experimentally investigated. Finally, we discussed these parameters based on different solvents for optoelectronic applications in detail.

2. Experimental details

2.1. The solutions of the PTCDI-C8 for various solvents

We purchased the PTCDI-C8 nanostructure material, which its fullname is *N*,*N*′-Dioctyl-3,4,9,10-perylenedicaroboximide, and solvents (ethanol, methanol and chloroform) from Sigma-Aldrich Co. We arranged the solutions of PTCDI-C8 nanostructure dissolved homogeneously in 8 mL volume of ethanol, methanol and chloroform solvents at 2.75 mM.

2.2. The UV-vis measurements

Then, we taken the UV–vis measurements of PTCDI-C8 solutions for different solvents using a Shimadzu Spectrophotometer (UV-1800, Japan) at room temperature.

2.3. Theoretical considerations

In here, we will give theoretical considerations for significant optical properties such as molar absorptivity (molar extinction coefficient), mass molar absorptivity (mass extinction coefficient), optical band gap, refractive index,

Molar absorptivity or molar extinction coefficient (ε) is an important optical parameter and plays role on UV–vis spectra of materials. The ε can be determined by Beer–Lambert law [32],

$$\varepsilon = \frac{\mathrm{Abs}}{\mathrm{cL}} \tag{1}$$

where Abs is absorbance, c is molar concentration and L is length of the optical path.

Mass is an efficient factor on molar absorptivity. Mass absorptivity or mass extinction coefficient (α_{mass}) gives molar extinction coefficient per unit molecular weight. The α_{mass} parameter is given by [33],

$$\alpha_{\mathrm{mass}} = \frac{\varepsilon}{\mathrm{M_A}} \tag{2}$$

where is M_A is the molecular weight.

Tauc model [34] estimates the optical transitions and optical band gap of materials. The optical band gap (E_g) is the most essential parameter of the optical parameters. The E_g of materials can be determined by Tauc model,

$$\alpha(\mathrm{E}) = \mathrm{A}(\mathrm{E} - \mathrm{E_g})^{\mathrm{n}} \tag{3}$$

where α is the absorption coefficient, E is photon energy, A is a constant. n determines the type of the optical transitions.

Refractive index (n) parameter is the most another esseintial parameter of the optical parameters and can be calculated based on reflectance (R) from the following equation,

$$\mathrm{n} = \sqrt{\frac{4\mathrm{R}}{(\mathrm{R}-1)^2} - \mathrm{k}^2} - \frac{\mathrm{R}+1}{\mathrm{R}-1} \tag{4}$$

where k depends on absorption coefficient and $k = \alpha\lambda/4\pi$.

There are two regions for refractive index dispersion including normal and abnormal dispersion region. The refractive index dispersion is analyzed with a multi oscillator model in abnormal region, while the refractive index dispersion is analyzed with a single oscillator model in normal region. The n dispersion is evaluated by the Wemple–DiDomenico equation [35,36],

$$\mathrm{n}^2 - 1 = \frac{\mathrm{E_0 E_d}}{\mathrm{E_0^2} - \mathrm{E}^2} \tag{5}$$

where E_0 is single oscillator energy (or average excitation energy) and E_d is dispersion energy.

M_{-1} and M_{-3} moments can be explained depending on single oscillator and dispersion energy and is given by [37],

$$\mathrm{M_{-1}} = \mathrm{M_{-3}} \mathrm{E_0^2} \tag{6}$$

and

$$\mathrm{M_{-3}} = \frac{\mathrm{M_{-1}^3}}{\mathrm{E_d^2}} \tag{7}$$

The optical oscillator strength (f) is another important parameter for optical transitions and is given by [36],

$$f = \mathrm{E_0 E_d} \tag{8}$$

The contrast (α_c) depends on normalised refractive index and shows the sensitivity of a material or device. The α_c is given by

$$\alpha_{\mathrm{c}} = 1 - \left(\frac{\mathrm{n_1}}{\mathrm{n_2}}\right)^2 \tag{9}$$

The surface and volume energy loss functions (SELF and VELF) depend on the dielectric constant are significant parameters. The SELF and VELF parameters can be determined with following equations [38],

$$SELF = \frac{\varepsilon_2^2}{(\varepsilon_1 + 1)^2 + \varepsilon_2^2} \tag{10}$$

and

$$VELF = \frac{\varepsilon_2^2}{\varepsilon_1^2 - \varepsilon_2^2} \tag{11}$$

where $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$ are the real and imaginary parts of the dielectric constant, respectively.

3. Computational details

The structural, electronic and spectroscopic properties of the PTCDI-C8 have been investigated using DFT [39] at the B3LYP level [40–42]. The 6-311G (d, p) basis set has been used in the calculations. In order to test the validity and reliability of our calculations, CAM-B3LYP [43] functional were also tested for accuracy and efficiency of the calculations because B3LYP actually